NDCEE

National Defense Center for Energy and Environment

Demonstration and Validation of *Multi-increment®* Sampling for Range Sustainability

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CTC/NDCEE

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NDCEE Sustainable Ranges Task: An Overview

- The NDCEE demonstrated/validated multi-increment® sampling (MIS) in conjunction with U.S. EPA Method 8330B, as a tool for DoD site assessment.

- MIS and 8330B is a more reproducible, cost efficient, and reliable means of soil sample analysis to improve the environmental quality and ultimately sustainability of DoD Ranges.

Background

- Chemical energetic and propellant residues from detonation or manufacture of munitions and explosives of concern (MEC) at DoD sites may affect both the environment and human health.

- DoD sites potentially contaminated with munitions constituents:
  - Ammunition Plants
  - Training Ranges
  - Demolition Sites
  - Ammunition Test Sites
  - Storage Areas.

- DoD environmental safety must be maintained during:
  - Transition of land from government to public use
  - Site encroachment from residential housing, industrial growth, and expanding agricultural lands.

Background (Cont'd.)

Readiness and Environmental Protection Initiative Second Annual Report to Congress (May 2008)

Submitted by the Deputy Under Secretary of Defense for Installations & Environment On behalf of the Office of the Secretary of Defense

"…when population growth and resulting development increase near and around military bases, so do potential land-use conflicts between mission activities and local communities. In many cases, training or testing opportunities may be postponed, restricted, or even eliminated."

Improvement Continues in DOD's Reporting on Sustainable Ranges, but Opportunities Exist to Improve Its Range Assessments and Comprehensive Plan (Dec. 2008)

Government Accountability Office

"Department of Defense (DOD) training ranges and operating areas are required to be managed and operated to support their long-term viability and utility to meet the national defense mission."

REPI 2008

GAO

Accountability * Integrity * Reliability

b. PROGRAM ROLE AND CONTEXT

The Problem

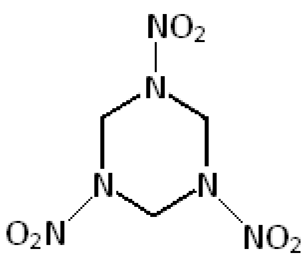
The United States military is being called upon to conduct increasingly complex and constantly evolving wartime operations around the globe. This mission demands sophisticated and flexible single-service, multi-service, and joint testing and training capabilities among the Military Services, combatant commands, and other DoD and non-DoD organizations. Realistic training and effective weapons systems testing measurably increase the survivability and success of our military forces in combat by ensuring the reliability and effectiveness of weapons systems and by providing the armed forces with the realistic, hands-on experience needed to ensure success in combat.

Figure 1.1 | Some of the factors of encroachment that restrict military operations and training capability as identified by DoD

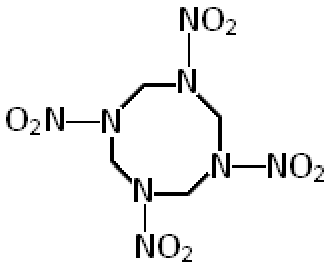
However, intensifying development and growing competition for land, air, sea and frequency spectrum resources, if left unchecked, will degrade training and testing activities, and thereby inhibit military readiness. In particular, when population growth and resulting development increase near and around military bases, so do potential land-use conflicts between mission activities and local communities. For instance, development near many military airports limits military flights to a narrow landing and takeoff corridor. Many military aircraft carrying heavy munitions cannot take off or land in narrow flight paths under some weather conditions, thereby

Background (Cont'd.)

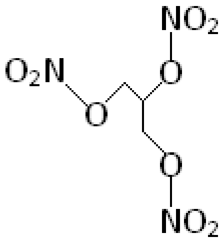
- Common Energetics and Propellants:
  - Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
  - Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)
  - Nitroglycerin (NG)
  - 2,4-Dinitrotoluene (DNT)
  - Trinitrotoluene (TNT).



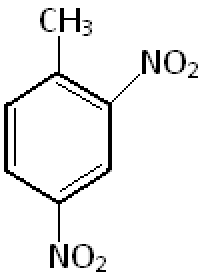
RDX



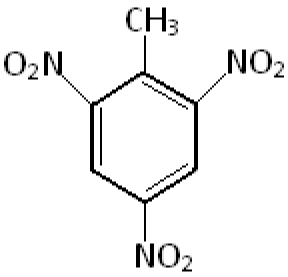
HMX



NG



DNT



TNT

Multi-increment® Sampling (MIS)

- Developed by EnviroStat, Inc. and studied by the U.S. Army Corps of Engineers Cold Regions Research and Engineering Laboratory (U.S. ACE CRREL) for characterization of a wide variety of ranges in varying climatic and soil conditions.

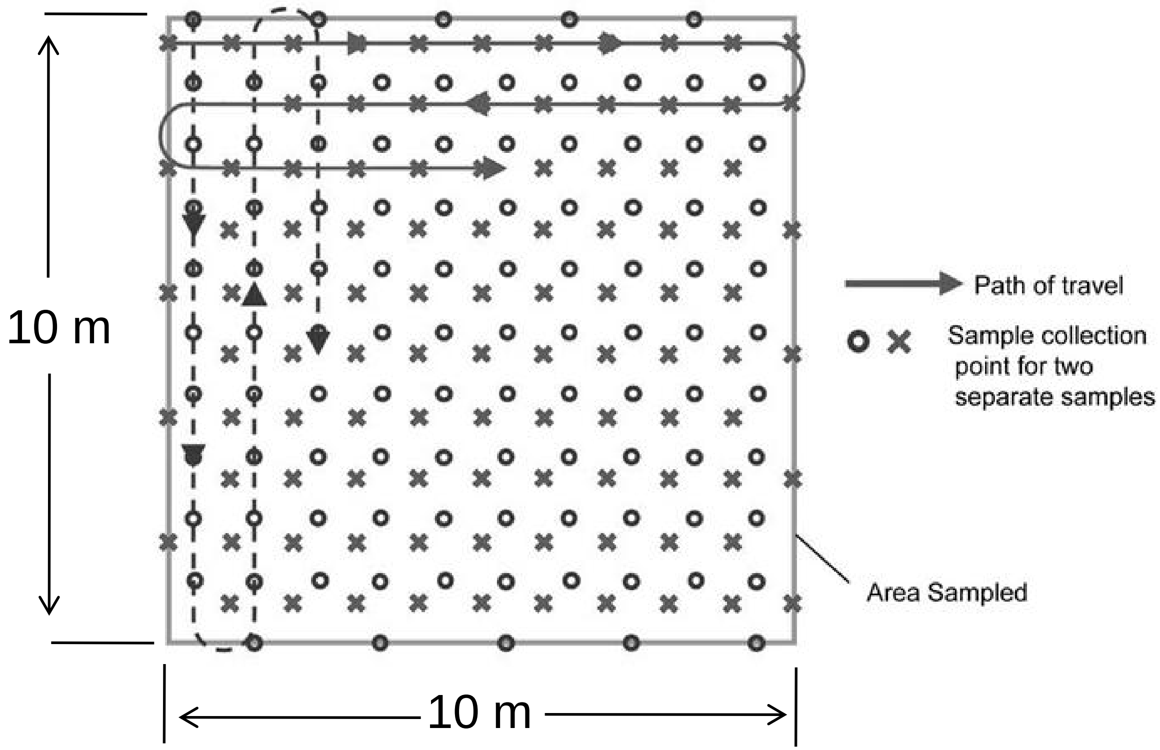
- Used to characterize the mean of the contaminant concentration in the decision unit (area of interest or exposure unit).

- Alternative surface soil sampling techniques often exhibit high standard deviation and skewed or non-reproducible results that do not provide solid evidence for decision making.

- MIS was developed to reduce the above issues noted with:
  - Discrete sampling
  - Composite sampling with limited increments.

MIS (Cont'd.)

- Considers all increments of a chosen area, or decision unit, as a whole.



MIS (Cont'd.)

- A decision unit is chosen to represent a specific exposure unit or area of interest; can be various shapes/sizes depending upon contamination source. Typically 100 m^2 minimum.
- Depths studied for range characterization are shallow – typically 0 to 2.5 cm depth interval sampled. Depth may exceed 2.5 cm.
- Typically, 30-100 increments are recommended per decision unit; number, depth, size of increments vary with decision unit size.
- Ultimately, around 1kg of soil will be sampled (per decision unit) and sent to the laboratory.

Tools needed for MIS (Jenkins, 2009)

U.S. EPA Method 8330B

- Involves air drying, sieving, and pulverizing the entire sample.
- Unique to Method 8330B is the whole sample processing and incremental subsampling of the pulverized sample.
- Approximately 30 increments will be collected to create the subsample for extraction.
- “Smaller particle size and a larger portion analyzed yields better precision.” (Bruce and Penfold, 2009).

Sites with Prior Use of MIS

- The following sites tested or used MIS in the early stages of development:
  - Kagman Former Airfield Dumpsite, Saipan
  - Dona Ana Range, Fort Bliss, New Mexico
  - Donnelly Training Area, Alaska
  - Eagle River Impact Area, Ft. Richardson, Alaska.
- MIS has since been studied and used at many additional sites and is the regulator's choice in several states in U.S. EPA Regions 9 and 10.

MIS Benefits

- MIS provides the following benefits:
  - Results more precise and accurate.
    - Mean concentration closer to the perceived actual mean
    - Smaller standard deviation among replicates
    - A high degree of sampling reproducibility
  - Cost effective
    - Reduced human and analytical error due to reduced number of samples
    - Reduced time performing field work (cost reduction)
    - Reduced analytical cost because fewer samples are needed to achieve reliable results.
  - MIS meets the three fundamental principles of soil sampling

Project Approach

- Sampling demonstrations at two diverse ranges - a live-fire bombing range with arid, sandy soils and a shoulder-fired grenade range with humid sandy loam soils
- Comparison of discrete, box, and wheel sampling methods to MIS
- Comparison of EPA Method 8330A (utilizing scoop off the top sampling) and EPA Method 8330B (whole sample processing)
- Preliminary assessment of two different EPA Method 8330B grinding methods (roller ball mill and ring and puck mill)
- Comparison of laboratory subsampling methods to bulk sample analysis
- Analysis of variance of field and laboratory sample replicates
- Cost Benefit Analysis.

NDCEE Demonstration/Validation

- Field sampling at Red Rio Bombing Range, Live Drop Impact Area, Holloman AFB completed March 24, 2009.
- Field sampling at shoulder-fired grenade launcher range, DoD site in the humid northwest region completed May 7, 2009 and July 28, 2009.
- Sample analysis being completed at TestAmerica Laboratories, Inc., Denver, CO.
- Full results are available for Holloman AFB and preliminary results are available for Fort Lewis.

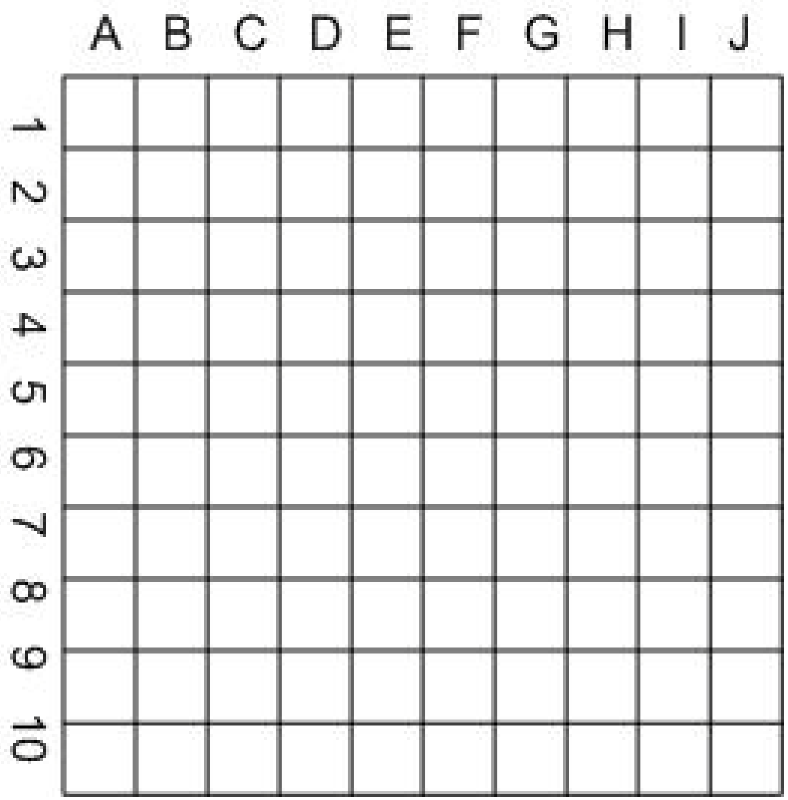
Collecting Increments (NDCEE, 2009)

Holloman AFB

Weathered Bomb (NDCEE, 2009)

Decision Unit Layout (NDCEE, 2009)

Holloman AFB Decision Unit



- 10 m x 10 m decision unit adjacent to crater of low order detonation of 500 pound bomb.
- Tritonal (2,4,6-Trinitrotoluene (TNT) with aluminum) prime contaminant of potential concern.
- Collected four field replicates each of discrete, box, wheel, MIS ball mill, and MIS puck mill samples.
- All samples 0 – 2.5 cm depth, dry, loose fine to coarse sand with very little vegetation.
- 100 increments collected for multi increment (MI) samples.

Data Evaluation

- Key concept is that true mean is unknowable; Assess representativeness by “reproducibility”, indicated by variance of data in like groups.
- Calculate mean and Standard Deviation (Std Dev) of each like data group.
- Calculate % Relative Standard Deviation (% RSD) of each like data group; Compare % RSDs (e.g. data resulting from “scoop off the top” vs. “in-lab MIS procedure”) % RSD = (s*100)/m.
- The lower the % RSD for a like data group, the better quality the data in terms of reproducibility, therefore representativeness.
  - Holloman Example: Field replicates % RSD MIS-Ball-HPLC/UV = 41.6%; % RSD Discrete = 170%
- Calculate Relative Percent Difference (RPD) to compare two values (e.g. subsample to bulk sample) RPD = ABS(A-B)/m*100.
  - Holloman Example: Mean of laboratory replicates to bulk results show 4.1% RPD for MIS-Ball-HPLC/UV and 87.8% RPD for Discrete

NDCEE Dem/Val Holloman AFB Results

Holloman Data TNT (mg/kg), Laboratory Replicates Comparison

Sample Type	Replicates			Bulk	Mean	Range	Std Dev	% RSD	Rel % Diff	Range % diff		RSD Rank	RPD Rank
	1	2	3							High	Low		
Discrete	1900	230	210	2000	780	210-1900	970	124	-87.8	-5.1	-162	7	7
Box	1100	1800	1500	3300	1467	1100-1800	351	23.9	-76.9	-58.8	-100	5	6
Wheel	0.6	0.37	0.47	0.8	0.48	0.37-0.6	0.12	24.0	-50.0	-28.6	-73.5	6	5
MIS-Ball-HPLC	1700	1700	1600	1600	1667	1600-1700	57.7	**3.46**	**4.1**	6.1	0.0	1	1
MIS-Ball-MS/MS	1600	1300	1400	1600	1433	1300-1600	153	**10.7**	**-11.0**	0.0	-20.7	3	3
MIS-Puck-HPLC	1500	1400	1700	1900	1533	1400-1700	153	**9.96**	**-21.4**	-11.1	-30.3	2	4
MIS-Puck-MS/MS	1600	1400	1800	1500	1600	1400-1800	200	**12.5**	**6.5**	18.2	-6.9	4	2
Rule of Thumb: RSD for laboratory replicates should be <20% for MIS (Rieck, 2008)													

NDCEE Dem/Val Holloman AFB Results (Cont'd.)

Holloman Data TNT (mg/kg), Field Sampling Comparison

Sample Type	Replicates				Mean	Range	Std Dev	% RSD	RSD Rank
	1	**2**	**3**	**4**					
Discrete	1900	11	37	200	537	11-1900	913	170	6
Box	1100	160	6400	3700	2840	160-6400	2810	98.9	5
Wheel	0.6	21000	42	90	5280	0.60-21000	10500	199	7
MIS-Ball-HPLC	1700	1300	2000	3300	2080	1300-3300	866	**41.6**	3
MIS-Ball-MS/MS	1600	1100	1500	2900	1780	1100-2900	780	**43.8**	4
MIS-Puck-HPLC	1500	2100	1000	1700	1580	1000-2100	457	**28.9**	1
MIS-Puck-MS/MS	1600	2300	1100	1500	1630	1100-2300	499	**30.6**	2
Rule of Thumb: RSD for Field Replicates should be <30% for MIS (Rieck, 2008)									

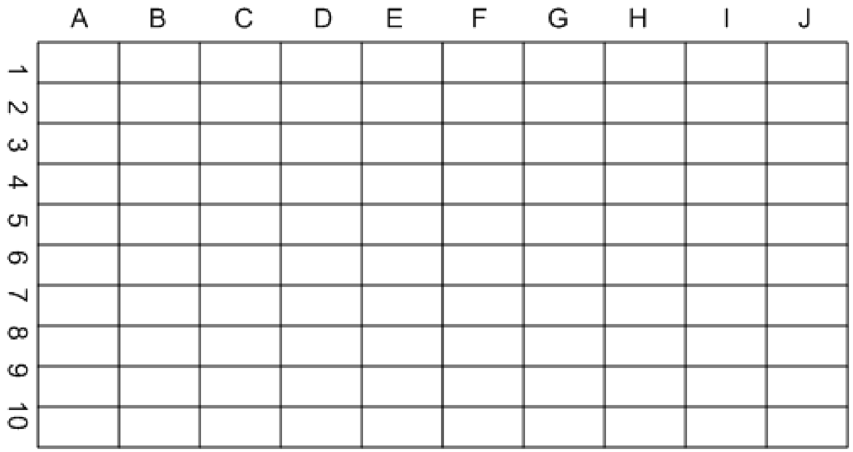
Sampling at Fort Lewis

Entering Range Area (NDCEE, 2009)

Decision Unit Layout (NDCEE, 2009)

Fort Lewis Decision Unit

- 20 m x 10 m decision unit behind firing points of shoulder-fired LAW rockets.
- Nitroglycerin (NG) prime contaminant of potential concern.
- Collected four field replicates each of discrete, box, wheel, MIS ball mill, and MIS puck mill samples.
- All samples 0 – 2.5 cm depth, well-drained sandy loam soils.



- 100 increments collected for MI samples.
- First data resulted in MIS-Ball sample loss in lab; resampling recently completed

NDCEE Dem/Val Preliminary Fort Lewis Results

Ft. Lewis Data NG (mg/kg), Laboratory Reps Comparison

Sample Type	Replicates			Bulk	Mean	Range	Std Dev	% RSD	Rel % Diff	Range % diff		RSD Rank	RPD Rank
	1	2	3							High	Low		
Discrete	632	691	667	467	663	632-691	29.7	4.47	34.7	38.7	35.3	3	6
Box	914	870	952	594	912	870-952	41.0	4.50	42.2	46.3	37.7	4	7
Wheel	986	960	1230	815	1059	960-1230	149	14.1	26.0	40.6	16.3	7	5
MIS-Ball-HPLC	765	756	762	832	761	756-765	4.58	**0.60**	**-8.9**	-8.4	-9.6	1	2
MIS-Ball-MS/MS	807	755	733	654	765	733-807	38.0	**4.97**	**15.6**	20.9	11.4	5	4
MIS-Puck-HPLC	803	826	787	729	805	787-826	19.6	**2.43**	**10.0**	12.5	7.7	2	3
MIS-Puck-MS/MS	735	797	846	761	793	735-846	55.6	**7.02**	**4.1**	10.6	-3.5	6	1

Rule of Thumb: RSD for laboratory replicates should be <20% for MIS (Rieck, 2008)

NDCEE Dem/Val Preliminary Fort Lewis Results (Cont'd.)

Ft. Lewis Data NG (mg/kg), Field Sampling Comparison

Sample Type	Replicates				Mean	Range	Std Dev	% RSD	RSD Rank
	1	2	3	4					
Discrete	632	805	248	1150	709	248-1150	375	52.9	6
Box	914	597	1120	765	849	597-1120	222	26.2	5
Wheel	986	2760	457	687	1220	457-2760	1050	86.1	7
MIS-Ball-HPLC	765	753	802	738	765	738-802	22.6	**2.96**	1
MIS-Ball-MS/MS	807	762	751	676	749	676-807	54.4	**7.26**	3
MIS-Puck-HPLC	803	889	893	865	863	803-893	41.5	**4.82**	2
MIS-Puck-MS/MS	735	872	931	826	841	735-931	82.7	**9.83**	4

MIS-Ball results estimated due to incomplete sample analysis in lab; Resampling completed July 2009.

Rule of Thumb: RSD for Field Replicates should be <30% for MIS (Rieck, 2008)

NDCEE Dem/Val Results

- <u>In the field</u>:
  - MIS procedures resulted in much better reproducibility for field replicates than discrete, box, or wheel methods, close to 30% RSD goal except at extremely heterogeneous site.
  - MIS provided superior samples:
    - At Holloman AFB bombing range, with scattered titronal (TNT with aluminum) chunks on the surface of non-vegetated arid sandy soils.
    - At Fort Lewis firing points, with microscopic NG embedded in nitrocellulose fibers in grassy, humid sandy loam soils.
  - MIS procedures provide data more representative of the true mean of the contaminant concentration within the decision unit, based on the smaller variance between the field replicates (total sampling error).

NDCEE Dem/Val Results (Cont'd.)

- In the laboratory:
  - MIS subsampling procedure (Method 8330B) led to superior reproducibility for lab replicates compared to scoop off the top and mortar and pestle grinding (Method 8330A).
  - MIS subsamples provided a more representative subsample in comparison to the bulk sample analysis over the scoop off the top method at Holloman AFB and Fort Lewis.
  - For crystalline energetics such as TNT, roller ball mill and ring and puck mill grinding methods may be roughly equivalent in effectiveness. The puck mill may be more effective for contaminants found in nitrocellulose fibers such as NG, though dem/val final results are still out.

NDCEE Dem/Val Results (Cont'd.)

- <u>In the laboratory (cont'd.):</u>
  - UV detection appeared to provide slightly better reproducibility than MS/MS. MS/MS may be favored in some cases regardless, including when lower detection limits are needed, and for complex sample matrices (Penfold, 2008).

NDCEE Dem/Val CBA Results

- Cost comparisons based on three replicate MIS samples compared to 30 discrete samples assumed to provide equivalent data, based on previous research.
- Labor cost:
  - Lower for MIS compared to discrete sampling method that could yield equivalent quality data. With a coring tool, 100 MIS increments plus replicates take about the same time as a few discrete samples. For one 100 m^2 decision unit, a two-person team may take twice as much time to collect 30 discrete samples as to collect three replicate 100-increment MI samples.
- Analytical cost savings:
  - With MIS, fewer analyses required to yield equivalent data
  - For single 100 m^2 decision unit, analytical cost > 3x higher for 30 discrete samples than for three MI sample replicates, including appropriate laboratory quality control samples.
  - Offsets higher shipping costs for larger samples and use of 8330B instead of 8330A.
- Overall cost 189% higher for 30 discrete samples compared to three MI sample replicates for single decision unit.
- Indirect cost benefits may result from higher confidence in reproducible results:
  - Reduced demand for confirmation sampling
  - More straight-forward decision process.

Project Proven MIS Benefits

- MIS did, in fact, prove these benefits:
  - Results more precise and accurate
  - Mean concentration closer to the perceived actual mean
  - Smaller standard deviation among replicates
  - A high degree of sampling reproducibility
  - Cost effective
  - Reduced human and analytical error due to reduced number of samples
  - Reduced time performing field work (cost reduction)
  - Reduced analytical cost because fewer samples were needed to achieve reliable results.

Project Proven MIS Benefits (Cont'd.)

- Most importantly, MIS meets the three fundamental principles of soil sampling:
  - Accurate representation of the mean constituent concentrations in the decision unit
  - High level of confidence for decision making
  - Cost reduction for similarly accurate results compared to other methods.

MIS Limitations

- DoD research focused primarily on application for shallow surface soil sampling at ranges.
  - Application for contaminants other than energetics residues limited to date; metal co-contaminants can not yet be evaluated alongside – potential grinding impacts.
  - Some depth profiling completed (apparent cost savings likely decrease with depth unless drilling).
- Goal must be to determine mean concentration of contaminant in area of interest.
  - MIS has better chance of including hotspots in an MI sample than typically discrete sampling, however the mean concentration overall will be what is determined.
- MIS in field must go hand in hand with whole sample analysis in laboratory (Laboratory protocols must be examined to ensure compatibility with MI sampling).

Future of MIS

- Continued studies of MIS in the sustainability of DoD sites.
- Expanding use of MIS to include metals and other contaminants (Environmental Security Technology Certification Program (ESTCP) New Start 2009 project to develop MIS protcols for metals); Among parameters to be considered:
  - Impact of grinding
  - Whole sample processing
  - Sampling depth.
- Expanding list of regulatory authorities approving or requiring MIS for range characterization.
- The Interstate Technology and Regulatory Council (ITRC) Incremental Sampling team will report on its work in 2010. The report by this coalition of regulatory groups will enhance the MIS approval process for an expanded list of parameters.

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